Inorganic Chemistry
Article
pubs.acs.org/IC

Nitrogen-rich Compounds of the Actinoids: Dioxouranium(VI) 5,5′-Azobis[tetrazolide] Pentahydrate and Its Unusually Small Uranyl Angle

Georg Steinhauser,*,[†] Gerald Giester,[‡] Christoph Wagner,[§] Peter Weinberger,[⊥] Bernhard Zachhuber,[§] Georg Ramer,[§] Mario Villa,[†] and Bernhard Lendl[§]

[†]Vienna University of Technology, Atominstitut, Stadionallee 2, 1020 Vienna, Austria
[‡]University of Vienna, Institute of Mineralogy and Crystallography, Althanstr. 14, 1090 Vienna, Austria
[§]Vienna University of Technology, Institute of Chemical Technologies and Analytics, Getreidemarkt 9/164, 1060 Vienna, Austria
[⊥]Vienna University of Technology, Institute of Applied Synthetic Chemistry, Getreidemarkt 9/163, 1060 Vienna, Austria

Supporting Information

ABSTRACT: Uranyl(VI) 5,5′-azobis[tetrazolide] pentahydrate was synthesized and characterized using X-ray crystallography, elemental analysis, UV/vis, MIR, FIR, and Raman spectroscopy. It is the second-most nitrogen rich compound of uranium (26.72 wt % N) and only the second structurally characterized uranium complex with a tetrazole ligand described in the literature. The compound's structure is characterized by an exceptionally small uranyl angle of 172.4(1)°, which provides information on the coordination properties of tetrazole ligands as they affect the donor's environment by strong steric and perhaps electrostatic repulsion. The compound showed luminescence under excitation with a near UV laser. The mean lifetime of its excited state was shorter than in the case of $UO_2(NO_3)_2 \cdot 6H_2O$, indicating quenching by the ligand. Despite its high nitrogen content (and thus potentially explosive character), the title compound proved to be stable even under neutron radiation causing induced fission processes.

Energetic materials based on nitrogen-rich compounds are a rapidly expanding scientific field, even beyond classic applications as explosives[1,2] and pyrotechnics.[3] 5-Substituted tetrazole derivatives or 3,6-disubstituted tetrazine derivatives have been discovered as precursors for the production of special materials such as nanostructured metal foams or nanoparticles of carbon or carbon nitrides by decomposition under inert conditions.[4−7] Related mechanisms yield uranium nitrides by decomposition of nitrogen-rich uranium compounds. Apart from other possible applications (such as N-atom transfer reactions and aziridination of small molecules), uranium nitrides may act as a potentially suitable nuclear fuel material.[8−14] Uranium nitrides are characterized by favorable nuclear properties, high stability, and thermal conductivity as well as a high melting point.[15] Also accelerator-driven transmutation of minor actinides may be conducted based on nitride matrices.[16] In particular fast breeder systems (which will become of increasing interest in the course of the development of Generation IV reactors) may benefit from these material properties as they are superior as compared to metallic fuels.[17] There are numerous conventional methods for the production of UN (carbothermic reduction as the most common in industrial applications, sol−gel methods, and others), which are summarized in ref 12. Apart from these methods, nitrogen-rich uranium compounds have been topic of recent research due to possible applications as precursors for the production of nitrido complexes of uranium or even UN fuel,[8,13,18] which explains the increasing interest in nitrogen-rich U compounds (although uranyl compounds may be difficult in this respect due to their thermodynamical stability). The Fukushima reactor accident showed the need for continuous innovation in the nuclear fuel sector improving the cooling properties of the fuel in case of reduced or emergency cooling. UN may be a promising alternative to conventional UO_2 nuclear fuel.

In this work, we present the synthesis, crystal structure, UV/vis, and vibrational spectroscopic characterization of a highly energetic uranium compound, uranyl(VI) 5,5′-azobis[tetrazolide] (ZT) pentahydrate ($UO_2(ZT) \cdot 5H_2O$; **1**), and thereby, the second-most nitrogen rich compound of uranium ever structurally characterized. Previous works on ZT compounds of the lanthanoids[19−22] revealed interesting coordination modes between the ZT^{2-} dianion and the cations

Received: February 20, 2012
Published: May 31, 2012

dx.doi.org/10.1021/ic300377j | *Inorg. Chem.* 2012, 51, 6739−6745

and hence acted as another motivation to investigate this behavior with the actinoids as well.

■ EXPERIMENTAL SECTION

CAUTION! *Salts of ZT (especially if anhydrous) are potentially sensitive energetic substances that can explode violently upon various stimulation such as heating, impact, friction, or electrostatic discharge. The use of safety equipment such as Kevlar gloves, wrist protectors, face shields, conducting shoes, and ear plugs is strongly recommended when handling such substances.*[23,24] *The work with energetic compounds of actinides should be done by experienced personnel and in properly equipped radiochemical laboratories.*

Instrumentation and Measurement. Raman spectra were collected on a micro-Raman spectrometer *LabRam HR800* (*Horiba Jobin Yvon*) equipped with a charge coupled detector (CCD) and a HeNe laser emitting at 632.8 nm with power set to 14.5 mW at 25 °C; slit width 100 μm, ensuring a spectral resolution of approximately 4 cm^{-1}; $\tilde{\nu}$ in inverse centimeters; relative intensities in percent of the most intense peak. IR spectra were recorded on a *Bruker-Tensor-27* (Pike Miracle Diamond-ATR, 1 reflection, and KBr pellet) between 4000 and 600 cm^{-1} with a resolution of 4 cm^{-1}; $\tilde{\nu}$ in inverse centimeters. FIR: Perkin-Elmer Spectrum 400 between 700 and 30 cm^{-1}, 1000 scans data acquisition. UV−vis−NIR: solid state electronic spectra have been acquired in diffuse reflectance using a *Perkin-Elmer Lambda 900* between 3300 and 190 nm; scan speed 125 nm/min. Elemental analyses (CHN): *Perkin-Elmer-2400* CHN Elemental Analyzer, property of the University of Vienna; values in weight percent. The isotopic composition of uranium was determined by using a Perkin-Elmer Elan DRC II ICP-MS. Single-crystal X-ray diffraction data (max. $2\Theta = 61°$) were collected on a Nonius KappaCCD diffractometer (graphite monochromatized Mo $K\alpha$-radiation, $\lambda = 0.71073$ Å) equipped with a 0.3 mm monocapillary optics collimator in a measurement at 200 K. For structure solution by direct methods and the structure refinements, the programs SHELXS-97[25] and SHELXL-97[26] were used, respectively. Absorption correction was done by evaluation of partial multiscans.

The experimental setup for the recording of the luminescence spectra of **1**, **2**, and $UO_2(NO_3)_2{\cdot}6H_2O$ consisted of a Q-switched Nd:YAG Laser (EKSPLA, Lithuania) fitted with a second and third harmonic generation crystal to emit 10 pulsed laser beams per second with a duration of 4.4 ns and a wavelength of 355 nm. In more detail, the setup is described elsewhere.[27] The laser beams had an average energy of 5.6 mJ, and an average diameter of 6 mm. The sample was placed in a 0.5 cm quartz glass cuvette and excited with the aforementioned laser. The light emitted by the sample was collected with a Schmitt-Cassegrain telescope (Celestron) with an aperture diameter of 6 in. and analyzed in a spectrometer consisting of an Acton standard series SP-2750 spectrograph (Princeton Instruments, NJ, USA) and a PI-MAX 1024RB intensified CCD (iCCD) camera (Roper, FL, USA). The time between the emission of the laser beam and the beginning of the data collection (delay) as well as the duration of the data collection (gate) could be set via a PC. The CCD detector also allowed accumulating multiple measurements on the chip before digitalization and thus to increase the signal-to-noise ratio. The sample was placed about 6 m from the telescope and the laser.

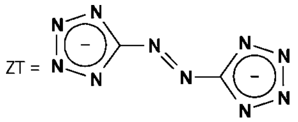
Procedure for Luminescence Measurements. Spectra of **1**, **2**, and UO_2ZT were collected with a gate of 200 ns and 25 on-chip accumulations per spectrum. In order to measure the intensity of the light emitted by the samples at different times after the excitation, several measurements with different delays were taken of all samples. The position of the measured emission overlaps with the second harmonic (532 nm) of the used Nd:YAG laser (1064 nm). Since the emission of $UO_2(NO_3)_2$ is comparably long-lived, it was possible to increase the delay enough to collect a spectrum of that sample without the second harmonic of the laser, in the spectra of the other samples this overtone is still visible as a sharp line at 532 nm.

Synthesis and Characterization. The starting material sodium 5,5′-azobis[tetrazolide] dihydrate $Na_2ZT{\cdot}2H_2O$ (**2**) was prepared by oxidation of 5-aminotetrazole with potassium permanganate in aqueous solution of sodium hydroxide; see ref 20 and references therein. $C_2H_4N_{10}O_2Na_2$ (246.099) calcd: C 9.76, H 1.64, N 56.91%; found: C 9.71, H 1.77, N 56.02%. To a solution of 100 mg $Na_2ZT{\cdot}2H_2O$ (0.41 mmol) in 2.5 mL H_2O, a solution of 204.7 mg $UO_2(NO_3)_2{\cdot}6H_2O$ (0.41 mmol) in 1.5 mL H_2O was added at room temperature. The reaction mixture turned dark yellow or orange immediately and was stored in a refrigerator at 4 °C. After 10 days, a significant amount of yellow crystals had formed on the bottom of the plastic vial, from where they were removed, washed with cold H_2O and acetone, and air-dried. Yield: 74% (159 mg) of pure, crystalline product. Anal. Calc. for $C_2H_{10}N_{10}O_7U$: C 4.58; H 1.92; N 26.72. Found: C 4.87; H 1.67; N 26.92. IR data for **1** (Diamond-ATR, KBr, and PE cm^{-1}): 3530 (vs), 3310 (sh), 3500−2500 (broad), 1649 (s), 1406 (vs), 1402 (sh), 1395 (sh), 1225 (m), 1203 (m), 1187(m), 1103 (w), 1096 (vw), 1089 (w), 945 (vs), 866 (sh), 821 (s), 774 (s), 741 (vs), 706 (s), 254 (m), 185 (m), 113 (m), 71 (m). Raman data for **1** (25 °C, cm^{-1}; relative intensities in percent): 1486 (61), 1402 (75), 1393 (100), 1113 (96), 1093 (15), 925 (9), 859 (16), 725 (1), 381 (1), 333 (2), 239 (3), 176 (2), 145 (2). Crystal data for **1**: Space group $P2_1/n$ (no. 14); $a = 8.977(1)$ Å, $b = 6.9420(5)$ Å, $c = 20.740(2)$ Å, $\beta = 96.665(5)°$, $V = 1283.7(2)$ Å^3, $T = 200$ K, $Z = 4$, $D_c = 2.712$ g cm^{-3}, $F(000) = 960$, $\lambda = 0.71073$ Å, 14498 reflections collected, 3897 independent reflections R_1 ($I > 2\sigma(I)$) = 0.024, wR_2 ($I > 2\sigma(I)$) = 0.042, R_1 (all data) = 0.040, wR_2 (all data) = 0.045, GOOF = 1.047, CCDC 755913.

■ RESULTS AND DISCUSSION

Synthesis. Compound **1** was synthesized in a straightforward reaction using aqueous solutions of uranyl(VI) nitrate hexahydrate and sodium 5,5′-azobis[tetrazolide] dihydrate (**2**), following eq 1.

$$Na_2ZT{\cdot}2H_2O + UO_2(NO_3)_2{\cdot}6H_2O \rightarrow UO_2(ZT){\cdot}5H_2O \downarrow + 2NaNO_3 + 3H_2O \quad (1)$$



In a preliminary experiment, it could be observed that at a temperature of approximately 80 °C, decomposition of the ZT^{2-} anion takes place in aqueous solutions containing both this anion and the UO_2^{2+} cation. As a result of this decomposition reaction, a dark brown precipitate was formed and gas evolved, similar to what has been described previously in a reaction using $Ce(SO_4)_2$ and Na_2ZT.[28] Therefore, the reaction mixture was immediately cooled in a refrigerator at 4 °C. The crystalline compound proved to be very stable over time. It was completely characterized by elemental analysis, X-ray crystallography, UV/vis, MIR, FIR, and Raman spectroscopy.

Crystal Structure Analysis. Compound **1** crystallizes in the monoclinic space group $P2_1/n$. Selected crystal data are given in Table 1.

The crystal structure revealed that the uranyl(VI) ion is surrounded by four H_2O molecules and by the N1 atom of the ZT ion to form a distorted pentagonal bipyramid (Figure 1a), which is common for uranyl complexes. An interesting rhombohedral uranium environment was reported previously.[29,30]

Following a uranyl(VI) 5-pyrimidyl-tetrazolate (UO_2-pmtz),[31] compound **1** is the second uranium(VI) compound with a tetrazole ligand ever reported in literature. It can be seen that the tetrazole ligand strongly affects the environment of

Table 1. Selected Crystal Data of 1

crystal data	1
formula	$C_2H_{10}N_{10}O_7U$
formula weight (g mol^{-1})	524.2
temperature (K)	200
crystal system	monoclinic
space group	$P2_1/n$ (no.14)
crystal dimensions (μm)	40 × 20 × 60
a (Å)	8.977(1)
b (Å)	6.9420(5)
c (Å)	20.740(2)
β (°)	96.665(5)
cell volume (Å^3)	1283.7(2)
Z	4
calc. density (g cm^{-3})	2.712
$R_1{}^a/wR_2{}^b$ (all data)	0.040/0.045
$R_1{}^a/wR_2{}^b$ ($I > 2\sigma(I)$)	0.024/0.042
GOOF	1.047

$^aR_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $^bR_w = [\sum(F_o{}^2 - F_c{}^2)/\sum w(F_o)^2]^{1/2}$.

uranium in this compound. The H_2O molecules that coordinate the uranium atom are shifted, "umbrella-like", to the opposite side of the tetrazole ring due to steric repulsion from the tetrazole ring. For the same reason, the O═U═O angle is compressed to 172.4(1)° compared to the ideal angle of 180°. This distortion of the uranyl angle exhibits the most interesting structural detail of this compound. The previously published UO_2-pmtz exhibits a similar distortion of the uranyl angle (174.7° and 173.4°); however, it is not as strong as **1** (in that case, and in contrast to compound **1**, one U atom is coordinated in a bidentate coordination mode of two N atoms of the tetrazole and the pyrimidine ligand). A reference to these angles is provided by the Cambridge Structural Database,[32] which evidenced for compound **1** the 12th smallest among more than 1400 uranyl angles (search range 160–180°); see Figure 2. It is interesting to note that many authors of such distorted angles did not comment on this unusual fact, e.g. refs 31, 33, and 34. Whereas in a study on uranyl complexes with nitrato and 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridine ligands,[35] the nonlinearity of the uranyl moiety was mainly explained with steric and electrostatic repulsions from the oxygen atoms of bidentate nitrato ligands, no such ligands are present in the case of compound **1** (and neither in ref 31), suggesting that the tetrazole ligand alone is able to induce such nonlinearities. In any case, distortions of the uranyl angle are not always caused by nitrogen-containing heterocycles, as in the case of uranyl complexes with cucurbit[6]uril, where the O═U═O angle was shifted to 172° by the oxygen atoms of large organic ligands.[34] In a classic paper, steric interactions of pyridine ligands and two uranium centers connected with an μ-oxo-bridge induced a distortion of the uranyl angle down to 171.5°.[36] Steric effects are also responsible for the aforementioned unusual rhombohedral configuration with the UO_2 moiety.[29,30]

A slight shift from the linear angle is a common phenomenon in uranium chemistry, as illustrated in Figure 2. The distortion of the $UO_2{}^{2+}$ angle observed in the structure of **1**, however, is

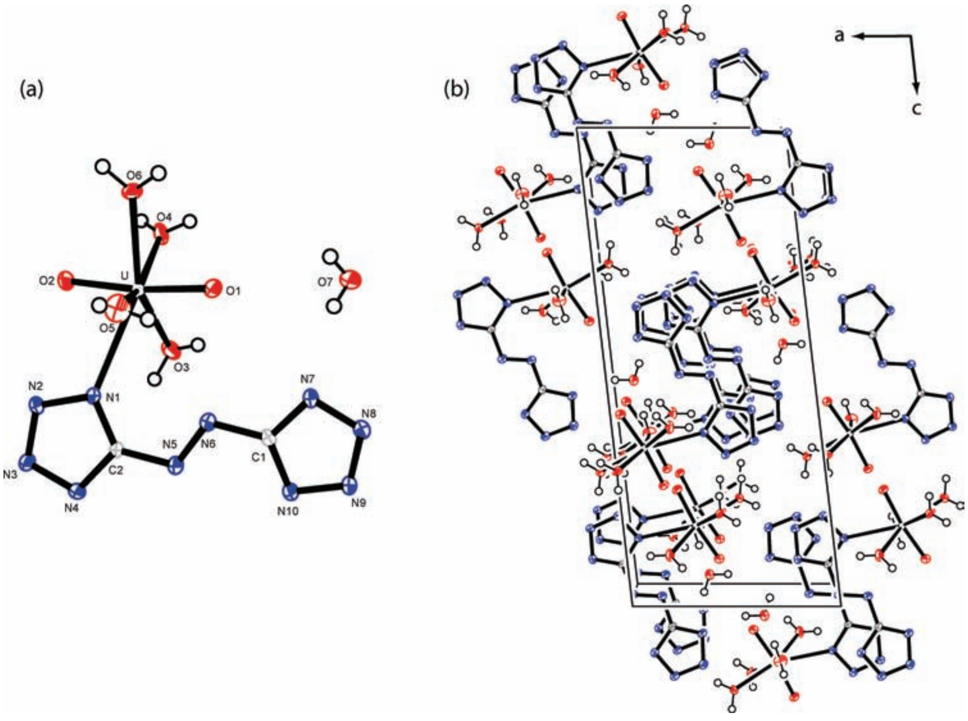


Figure 1. (a) Molecular structure determined from X-ray diffraction data and numbering scheme of 1 (thermal ellipsoids represent 50% probability). Selected bond lengths (Å): U–O1 1.756(2), U–O2 1.770(2), U–O4 2.357(3), U–O6 2.377(3), U–O5 2.380(3), U–O3 2.385(3), U–N1 2.656(3), N1–N2 1.339(3), N1–C2 1.341(4), N2–N3 1.327(4), N3–N4 1.336(4), N4–C2 1.333(4), N5–N6 1.264(4), N5–C2 1.399(4), N6–C1 1.408(4), N7–C1 1.329(4), N7–N8 1.334(4), N8–N9 1.329(4), N9–N10 1.328(3), N10–C1 1.344(4). Selected bond angles (deg): O1–U–O2 172.4(1), O1–U–O4 88.9(1), O1–U–O6 85.9(1), O1–U–O5 85.4(1), O1–U–O3 83.3(1), O1–U–N1 111.3(1), N2–N1–C2 104.0(2), N2–N1–U 121.7(2), C2–N1–U 133.7(2), N3–N2–N1 109.5(3), N2–N3–N4 109.6(2), C2–N4–N3 104.3(3), N6–N5–C2 112.5(3), N5–N6–C1 112.0(3), C1–N7–N8 103.9(3), N9–N8–N7 109.9 (2), N8–N9–N10 109.5(3), N9–N10–C1 104.0(3). (b) Crystal packing of **1** (in a perspectivic view approximately normal to (010); thermal ellipsoids represent 50% probability).

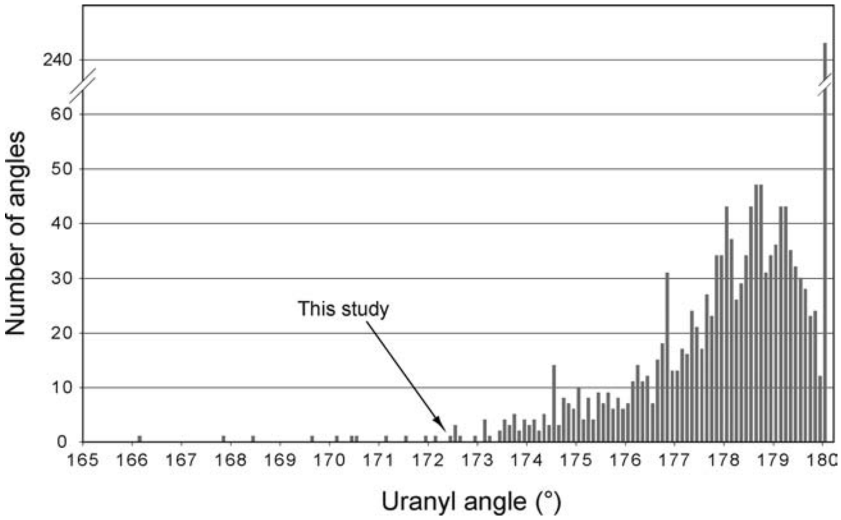


Figure 2. Uranyl angle distribution derived from 1453 hits in the Cambridge Structural Database. Eleven structures are reported with confirmed smaller angles than compound **1**.

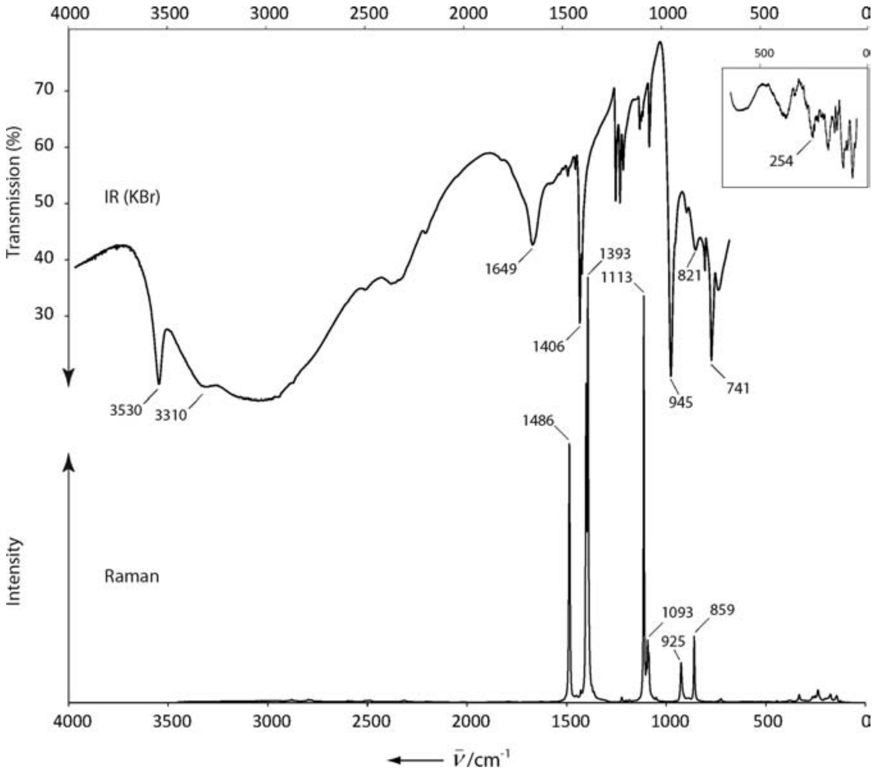


Figure 3. Vibrational spectra (Raman bottom, MIR top, FIR inset top) of compound **1**.

quite unusual. Structural features that deviate from the normal range of bonding in such way can help to assess the weaknesses and strengths of the models that are used to describe chemical bonds.[37]

Analysis of the hydrogen bonding system revealed D—A distances (A=O, N) in the range of 2.65 to 2.85 Å and D—H···A angles between 155 and 174° with the exception of O5—H51 with a bi- or trifurcated H-bond (D—A distances 2.98–3.16 Å).

The bond length of U–N1 of **1** (2.657(3) Å) is slightly longer than the U–N bond lengths of the previously published UO_2-pmtz (tetrazole ligand 2.626(6) and 2.519(7) Å; pyrimidyl ligand 2.714(7) Å)[31] or terpyridine complexes of uranyl,[38] slightly shorter than a previous paper[39] or roughly in the same range like previously reported uranium complexes with, e.g., triazacyclononane nitrogen-heterocycles,[40] bipyridine ligands,[29,41,42] and other nitrogen-containing heterocyclic ligands.[30,43]

The crystal packing of **1** is shown in Figure 1b. It can be described as a layered arrangement of $[UO_2(H_2O)_4]^{2+}$ cations in the O=U=O direction, intercalated with staggered layers of ZT anions. The U—N1 bond direction shows a zigzag structure, since the uranyl ions are alternately coordinated by ZT ions from the "inner" and "outer" ZT layer. The noncoordinating H_2O molecules are arranged between the $[UO_2(H_2O)_4]^{2+}$ moieties. H-bonds are also present between the H_2O molecules and the nitrogen atoms of the ZT anions and the oxygen atoms of the uranyl moieties.

Vibrational Spectroscopy. IR measurements showed the typical absorptions at 3530 cm^{-1} (asymmetric O7−H of the isolated H_2O molecule), a shoulder at 3310 cm^{-1} (symmetric O7−H of the isolated H_2O molecule), a broad absorption from 3500 to 2500 cm^{-1} (corresponding to the strongly coordinated H_2O ligands), 1649 cm^{-1} (H−O7−H bending of the isolated H_2O molecule), 1406 cm^{-1}, and 741 cm^{-1} of the ZT anion (slightly shifted to higher wavenumbers), correlating to the asymmetrical C2−N1 and C2−N4 stretching modes of the tetrazole ring, respectively.[44] Between 1350 and 700 cm^{-1} typical tetrazole ring vibrational modes are observed.[45] The bands at 945 and 821 cm^{-1} (stretching modes) are assigned to the uranyl moiety.[46,47] FIR measurements have been conducted in order to reveal the nonlinearity of the uranyl ion, according to ref 48. For a linear structure of the uranyl ion, the ν_2 mode is infrared inactive, whereas this mode should appear in the FIR spectra at around 250 cm^{-1} in a bent structure.[49] In fact, compound **1** exhibits a prominent IR absorption around 254 cm^{-1}, thus evidencing the nonlinearity of the uranyl moiety. Further vibrational modes in the low frequency range of the FIR are assigned to the "librational modes" of lattice H_2O.[48]

The ZT ion is extremely Raman active with several strong, characteristic bands[20,50] at, e.g., 1486 ($\nu_{sym}(N_{azo}{=}N_{azo})$), 1402 ($\nu_{as}(C{-}N_{ring})$), 1393 ($\nu_{sym}(C{-}N_{azo})$), 1113, 1093, and 925 cm^{-1}. This explains why other, weaker bands listed before appear as with a negligible intensity compared to those. However, they are still significant bands against the background. In addition to the typical ZT-bands, the symmetric stretching vibration (ν_{sym}) of UO_2^{2+} at 859 cm^{-1} (see ref 51) can be observed as a strong band in the Raman spectrum of **1**. According to the empirical correlation between the symmetric stretching frequency and the U=O bond length represented by eq 1a,[47,52]

$$R_{U=O} = (10650\nu^{-(2/3)}) + 57.5 \qquad (1a)$$

the title compound features a U=O bond length of 1.722 Å using the 859 cm^{-1} symmetric stretching vibration experimentally observed. This bond length value roughly fits the bond lengths of 1.770 and 1.756 Å, respectively, obtained by X-ray diffraction (Figure 1; see above).

Electronic Spectroscopy. UV−vis−NIR measurements of the solid powder sample reveal a broad band with a maximum around 420 nm as well as two more pronounced bands at 250 and 270 nm. The broad band around 420 nm can be identified as the O-to-U ligand to metal charge transfer (LMCT) band.[53] The bands around 250 and 270 nm are due to ligand absorptions. Two very strong and narrow bands around 330 and 370 nm are obviously related to the luminescence property of the sample (Figure 4; see below). Therefore, excitation close to these strong absorption bands can be used to probe the luminescence properties of the title compound.

Luminescence. It is known that the excited states of 4f elements often have long lifetimes giving rise to luminescent phenomena.[54] Consequently, investigations on the luminescent properties of 5f elements may appear promising.[31] The above-described absorption around 370 nm suggested the use of laser excitation in its close vicinity. A Nd:YAG laser (1064 nm) with a third harmonic generator yielding 355 nm was used. Under near UV excitation, all compounds (**1**, **2**, and $UO_2(NO_3)_2{\cdot}6H_2O$) show luminescence. The spectra of the three measured substances differ from each other in position and intensity of the bands (Figure 4). Another difference is the lifetime of the emission. Usually the time dependence of the intensity of luminescence is given by $I(t) = I_0 \exp(-(t/\tau))$, τ being the mean lifetime. The integral of the $UO_2(NO_3)_2$ band between 500 and 523 nm of spectra taken at different delays was plotted against the delay. From this plot, τ could be calculated via regression to be 448 ± 14 μs. The emissions of the two other substances had a much shorter lifetime; therefore, the expected exponential decay of the luminescence of these samples was overlapped in time by the pulse profile of the laser beam. Therefore no regression could be carried out.

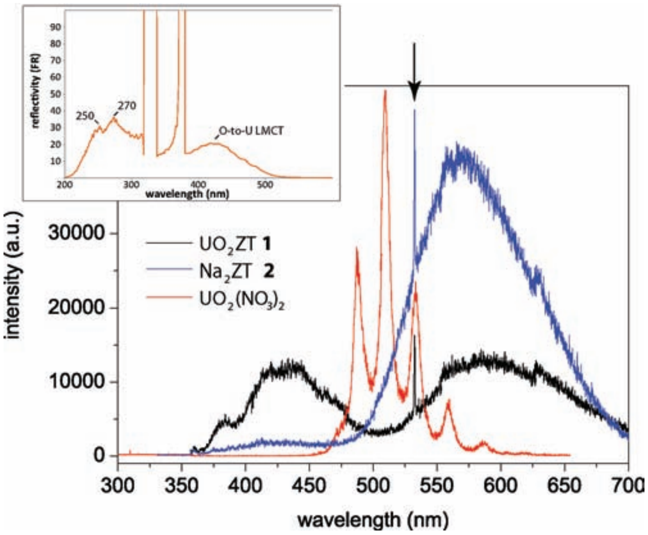


Figure 4. Absorption (inset) and luminescence spectra. Sample powders in quartz cuvettes excited with 355 nm laser (which coincides with the shoulder of a strong absorption band, see insert). The sharp signal at 532 nm in the spectra of **1** and **2** is caused by the remaining laser irradiation from the second harmonic of the used Nd:YAG laser (arrow).

Additionally to the significantly longer fluorescence lifetime of $UO_2(NO_3)_2$, the spectral features of this substance are much sharper than that for **1** and **2**, as illustrated in Figure 4.

Nuclear Properties. Nitrogen-rich, energetic compounds are routinely investigated with respect to stability criteria against external stimuli such as heat, friction, impact, electrostatic discharges, e.g. see refs 55 and 56. The performance of high explosives further can be investigated using the "Koenen" steel sleeve test, e.g. see ref 57. None of these sensitivity tests is advisible in the present case in order to not contaminate laboratory equipment with poisonous and radioactive U aerosols. To our knowledge, the stability of ZT compounds under ionizing radiation has never been investigated before. In this study, the stability of **1** against radiolytical decomposition was investigating, by exposing one crystal for 30 s to the neutron flux in a dry irradiation channel of the TRIGA Mark II research reactor at full power of 250 kW. The neutron flux density in this position is approximately 3 × 10^{12} cm^{-2} s^{-1}; the gamma dose rate during operation in this position cannot be measured with normal efforts, but it is certainly beyond the kilogray per hour range. The content of the fissile isotope ^{235}U in the utilized $UO_2(NO_3)_2$ raw material, as determined by ICP-MS, was slightly depleted (0.69% ^{235}U) compared with natural uranium (0.720% ^{235}U). Nuclear fission is the greatest internal stress that can be applied to matter. Of the total energy (approximately 200 MeV) set free per fission, some 170 MeV are transformed to kinetic energy of the fission products which fly apart at 3% of the speed of light. It is well-known that the fission products in solid, crystalline U-containing materials have an effective track length in the micrometer range (e.g., 20 μm in uranium-doped YBCO superconductors[58]), which means enormous stress to the crystalline integrity due to the ionizing power of these fragments. Nonetheless, using optical microscopy, it could be shown that the crystal was not affected by direct neutron and γ-irradiation or by fission-induced stress. Figure 5 shows the microscopic image crystal after irradiation, showing no signs of decomposition despite the applied radiative stress. This further approves the exceptional stability of crystalline hydrated ZT compounds.[20−22]

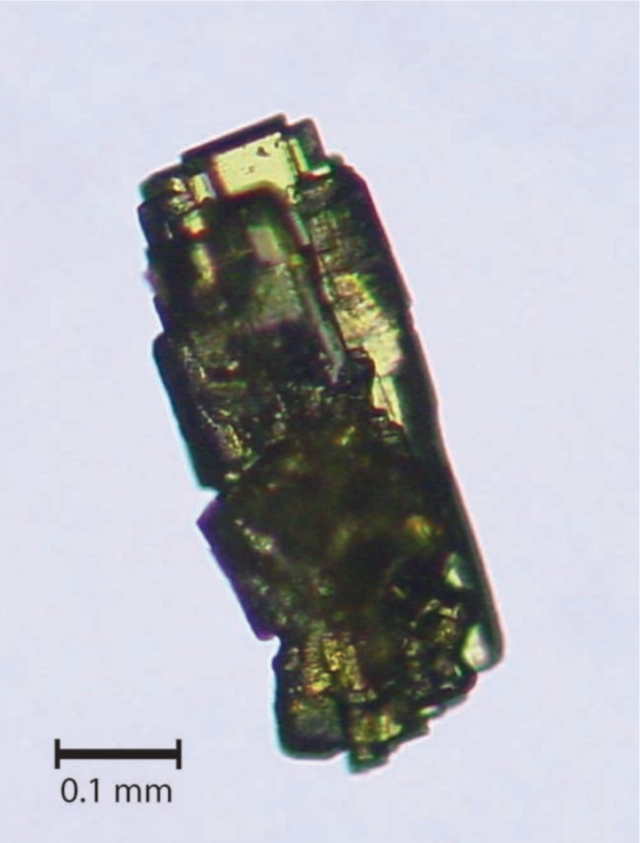


Figure 5. Microscopic image of **1** after neutron and gamma irradiation with focus on the top part of the crystal. No visible signs of decomposition can be spotted; the crystal remained entirely clear and in shape.

■ CONCLUSION

The title compound has been fully characterized, including crystal structure determination and vibrational spectroscopy. The ZT anion participates in the coordination sphere of the uranyl(VI) ion. To the authors' knowledge, it is one of the nitrogen-richest uranium compounds (26.72% N per weight) ever structurally characterized; only exceeded by a spectacular azido-compound.[8] The compound exhibits an unusually distorted O═U═O angle of 172.4°. The fundamental changes of the bonding within the uranyl moiety could be probed by vibrational as well as electronic spectroscopy.[52] In particular, the title compound shows a FIR absorption around 254 cm^{-1} giving evidence to the nonlinearity of the uranyl moiety. This is an independent physicochemical prove of the distortion of the O═U═O bond angle. A solid state powder UV−vis−NIR spectrum recorded in diffuse reflection reveals—despite of the expected absorption features giving rise to the color of the compound (ginger yellow)—a narrow sharp peak around 370 nm and allows for the selection of an appropriate excitation for luminescence investigations of compound **1**. The mean lifetime of the excited state is much shorter-lived than, e.g. $UO_2(NO_3)_2 \cdot 6H_2O$ (450 μs), indicating quenching caused by the ZT ligand. As nitrogen-rich compounds generally needed to be handled with care investigations on their stability against external stimuli are performed routinely. In this case, the presence of fissile ^{235}U allowed stability investigations under neutron bombardment. In spite of this enormous internal radiative stress the compound did not show any signs of decomposition, proving their exceptional stability.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in cif format. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for the structure of **1** have been deposited with the Cambridge Crystallographic Data Centre under the depository number 755913. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +43 1 58801 141389. Fax: +43 1 58801 14199. E-mail address: georg.steinhauser@ati.ac.at.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank Prof. Max Bichler for his support in the course of this study, Elzbieta Jorde for providing some of the essential chemicals from the TU Wien chemicals store, and Nicolae Leopold for performing the Raman measurements. We gratefully acknowledge financial support from the FP7 of the EU (OPTIX: Optical Technologies for the Identification of Explosives; FP7-SEC-2007-1 218037) and the Austrian Science Fund (FWF); P24955-N28. Furthermore we thank the Deans of the Faculties of Physics as well as of Technical Chemistry of the Vienna University of Technology for the acquisition of the ICP-MS.

■ REFERENCES

(1) Singh, R. P.; Verma, R. D.; Meshri, D. T.; Shreeve, J. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 3584−3601.

(2) Gao, H.; Shreeve, J. M. *Chem. Rev.* **2011**, *111*, 7377−7436.

(3) (a) Steinhauser, G.; Klapötke, T. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 3330−3347. (b) Steinhauser, G.; Klapötke, T. M. *J. Chem. Educ.* **2010**, *87*, 150−156.

(4) Chavez, D. E.; Hiskey, M. A.; Huynh, M. H.; Naud, D. L.; Son, S. F.; Tappan, B. C. *J. Pyrotech.* **2006**, *23*, 70−80.

(5) Huynh, M. H. V.; Hiskey, M. A.; Naud, D. L. Preparation of nanoporous metal foam from high nitrogen transition metal complexes. US Patent 2007142643 (priority application no. US 2006-604644), 2007.

(6) Tappan, B. C.; Huynh, M. H.; Hiskey, M. A.; Chavez, D. E.; Luther, E. P.; Mang, J. T.; Son, S. F. *Mater. Res. Soc. Symp. Proc.* **2006**, *896*, 15−24.

(7) Tappan, B. C.; Huynh, M. H.; Hiskey, M. A.; Chavez, D. E.; Luther, E. P.; Mang, J. T.; Son, S. F. *J. Am. Chem. Soc.* **2006**, *128*, 6589−6594.

(8) Nocton, G.; Pecaut, J.; Mazzanti, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 3040−3042.

(9) Thetford, R.; Mignanelli, M. *J. Nucl. Mater.* **2003**, *320*, 44−53.

(10) Black, L.; Miserque, F.; Gouder, T.; Havela, L.; Rebizant, J.; Wastin, F. *J. Alloy. Compd.* **2001**, *315*, 36−41.

(11) Fox, A. R.; Arnold, P. L.; Cummins, C. C. *J. Am. Chem. Soc.* **2010**, *132*, 3250−3251.

(12) Silva, G. W. C.; Yeamans, C. B.; Sattelberger, A. P.; Hartmann, T.; Cerefice, G. S.; Czerwinski, K. R. *Inorg. Chem.* **2009**, *48*, 10635−42.

(13) Fortier, S.; Wu, G.; Hayton, T. W. *Dalton Trans.* **2010**, *39*, 352−354.

(14) Fox, A. R.; Bart, S. C.; Meyer, K.; Cummins, C. C. *Nature (London, U. K.)* **2008**, *455*, 341−349.

(15) Arai, Y.; Minato, K. *J. Nucl. Mater.* **2005**, *344*, 180−185.

(16) Streit, M.; Ingold, F. *J. Eur. Ceram. Soc.* **2005**, *25*, 2687−2692.

(17) Mizutani, A.; Sekimoto, H. *Ann. Nucl. Energy* **1998**, *25*, 1011−1020.

(18) Fortier, S.; Wu, G.; Hayton, T. W. *J. Am. Chem. Soc.* **2010**, *132*, 6888−6889.

(19) Steinhauser, G. *Sitzungsber. Abteilung II (Trans. Austrian Acad. Sci.)* **2008**, *217*, 3−11.

(20) Steinhauser, G.; Giester, G.; Wagner, C.; Leopold, N.; Sterba, J. H.; Lendl, B.; Bichler, M. *Helv. Chim. Acta* **2009**, *92*, 1371−1384.

(21) Steinhauser, G.; Giester, G.; Leopold, N.; Wagner, C.; Villa, M. *Helv. Chim. Acta* **2009**, *92*, 2038−2051.

(22) Steinhauser, G.; Giester, G.; Leopold, N.; Wagner, C.; Villa, M.; Musilek, A. *Helv. Chim. Acta* **2010**, *93*, 183−202.

(23) Klapötke, T. M.; Krumm, B.; Steemann, F. X.; Steinhauser, G. *Saf. Sci.* **2010**, *48*, 28−34.

(24) Steinhauser, G.; Evers, J.; Jakob, S.; Klapötke, T. M.; Oehlinger, G. *Gold Bull.* **2008**, *41*, 305−317.

(25) Sheldrick, G. M. *SHELXS-97, a Program for the Solution of Crystal Structures*; University of Göttingen, Germany, 1997.

(26) Sheldrick, G. M. *SHELXL-97, a Program for Crystal Structure Refinement*; University of Göttingen, Germany: 1997.

(27) Zachhuber, B.; Ramer, G.; Hobro, A.; Chrysostom, E. t. H.; Lendl, B. *Anal. Bioanal. Chem.* **2011**, *400*, 2439−2447.

(28) Hammerl, A.; Holl, G.; Klapötke, T. M.; Mayer, P.; Noth, H.; Piotrowski, H.; Warchhold, M. *Eur. J. Inorg. Chem.* **2002**, 834−845.

(29) Berthet, J.-C.; Nierlich, M.; Ephritikhine, M. *Chem. Commun. (Cambridge, U. K.)* **2003**, 1660−1661.

(30) Berthet, J.-C.; Nierlich, M.; Ephritikhine, M. *Dalton Trans.* **2004**, 2814−2821.

(31) Rodriguez-Dieguez, A.; Mota, A. J.; Seco, J. M.; Palacios, M. A.; Romerosa, A.; Colacio, E. *Dalton Trans.* **2009**, 9578−9586.

(32) *Cambridge Structural Database (CSD version 5.29)*, March 2010.

(33) Aranda, M. A. G.; Cabeza, A.; Bruque, S.; Poojary, D. M.; Clearfield, A. *Inorg. Chem.* **1998**, *37*, 1827−1832.

(34) Thuery, P. *Cryst. Growth Des.* **2008**, *8*, 4132−4143.

(35) Berthet, J.-C.; Thuery, P.; Dognon, J.-P.; Guillaneux, D.; Ephritikhine, M. *Inorg. Chem.* **2008**, *47*, 6850−6862.

(36) Berthet, J. C.; Lance, M.; Nierlich, M.; Ephritikhine, M. *Eur. J. Inorg. Chem.* **2000**, 1969−1973.

(37) Göbel, M.; Tchitchanov, B. H.; Murray, J. S.; Politzer, P.; Klapötke, T. M. *Nat. Chem.* **2009**, *1*, 229−235.

(38) Charushnikova, I. A.; Den Auwer, C. *Russ. J. Coord. Chem.* **2007**, *33*, 53−60.

(39) Henry, N.; Lagrenee, M.; Loiseau, T.; Clavier, N.; Dacheux, N.; Abraham, F. *Inorg. Chem. Commun.* **2011**, *14*, 429−432.

(40) Castro-Rodriguez, I.; Olsen, K.; Gantzel, P.; Meyer, K. *J. Am. Chem. Soc.* **2003**, *125*, 4565−4571.

(41) Thuery, P. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2007**, *C63*, m54−m56.

(42) Borkowski, L. A.; Cahill, C. L. *Cryst. Growth Des.* **2006**, *6*, 2248−2259.

(43) Charushnikova, I. A.; Den Auwer, C. *Russ. J. Coord. Chem.* **2004**, *30*, 511−519.

(44) Jiao, B.-J.; Chen, S.-P.; Zhao, F.-Q.; Hu, R.-Z.; Gao, S.-L. *J. Hazard. Mater.* **2007**, *142*, 550−554.

(45) Klapötke, T. M.; Sabate, C. M. *Chem. Mater.* **2008**, *20*, 1750−1763.

(46) Bahgat, K. *Spectrochim. Acta, Part A* **2004**, *60A*, 1557−1562.

(47) Bartlett, J. R.; Cooney, R. P. *J. Mol. Struct.* **1989**, *193*, 295−300.

(48) Nakamotu, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4 ed.; Wiley: New York, 1986.

(49) Bullock, J. I.; Parrett, F. W. *Can. J. Chem.* **1970**, *48*, 3095−7.

(50) Darwich, C.; Klapötke, T. M.; Sabate, C. M. *Chem.—Eur. J.* **2008**, *14*, 5756−5771.

(51) Ruan, C.; Luo, W.; Wang, W.; Gu, B. *Anal. Chim. Acta* **2007**, *605*, 80−86.

(52) Denning, R. G. Electronic structure and bonding in actinyl ions. In *Complexes, Clusters and Crystal Chemistry (Structure and Bonding)*; Clarke, M. J., Ed.; Springer: Berlin, 1992.

(53) Sarsfield, M. J.; Helliwell, M. *J. Am. Chem. Soc.* **2004**, *126*, 1036−1037.

(54) Huang, C. *Rare Earth Coordination Chemistry*; John Wiley & Sons: Singapore, 2010.

(55) Fischer, N.; Goddard-Borger, E. D.; Greiner, R.; Klapötke, T. M.; Skelton, B. W.; Stierstorfer, J. *J. Org. Chem.* **2012**, *77*, 1760−4.

(56) Hammerl, A.; Holl, G.; Kaiser, M.; Klapötke, T. M.; Kranzle, R.; Vogt, M. *Z. Anorg. Allg. Chem.* **2002**, *628*, 322−325.

(57) Klapötke, T. M.; Stierstorfer, J. *Dalton Trans* **2009**, 643−53.

(58) Ren, Y.; Weinstein, R.; Sawh, R.-P.; Liu, J. *Physica C* **1997**, *282−287*, 2301−2302.